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(54) GELATINIZING AGENT OR SOLIDIFYING AGENT FOR ALCOHOL

(57)Abstract:

PURPOSE: To obtain a gelatinizing agent or solidifying agent useful as a solvent treating agent, a mold release agent, an adhesive, a binder, a sealing agent, etc., capable of forming a uniform, smooth, viscous and stable gelatinized or solidified material by adding a small amount of the gelatinizing agent or solidifying agent to an alcohol.

CONSTITUTION: This gelatinizing agent or solidifying agent for an alcohol liquid at a normal temperature (with the proviso that a ≥ 40 monohydric alcohol is omitted) comprises an esterification product of glycerol or its condensed substance, a 18-28C straight-chain saturated fatty acid and a 20-28C aliphatic saturated dibasic acid and the esterification product is a partial esterification product in which $>1/2$ hydroxyl groups of glycerol or its condensed material remain.

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CLAIMS

[Claim(s)]

[Claim 1] Gelation or the solidification agent of alcohol (however, with a carbon numbers of four or more monohydric alcohol is removed) liquefied in the ordinary temperature which consists of a partial esterification product which is an esterification product of a glycerol or its condensate, the straight chain-like saturated fatty acid of carbon numbers 18-28, and the aliphatic series saturation dibasic acid of carbon numbers 20-28, and was made to remain exceeding one half of the hydroxyl groups of said glycerol or its condensate.

[Claim 2] The gelation according to claim 1 or the solidification agent whose condensate of a glycerol is the thing of average degree of polymerization 5-10.

[Claim 3] The gelation according to claim 1 or the solidification agent whose liquefied alcohol is polyhydric alcohol, with a carbon number of less than four monohydric alcohol, or nitrogen-containing alcohol in ordinary temperature.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the esterification product which solidifies liquefied alcohol (however, with a carbon numbers of four or more monohydric alcohol is removed) in ordinary temperature. Gelation or the solidification agent of this invention can be used in the processing fields, such as the electrical and electric equipment, an electron, the device for MAG, a machine, an automobile, the miscellaneous goods for days, a color, ink, a coating, cosmetics, toiletries, drugs, agriculture, fishery, feed, the food field and paper, fiber, leather, resin, a macromolecule, rubber, and a metal, etc.

[0002]

[Description of the Prior Art] Conventionally, the metal soap of (1) higher fatty acid, 12-hydroxy stearin acid, a JIBEN zylidene sorbitol, JIBEN zylidene xylitol, a N-acylamino acid derivative, (2) dextrin fatty acid ester, an acrylic-acid system polymer, etc. are known as what has the function which solidifies fats and oils, a hydrocarbon, or a solvent to gel.

[0003] Among these, the type of (1) solidifies the whole to gel by making it dissolve or distribute in liquefied ester and fats and oils, and mainly cooling to homogeneity, at them. this gelling agent — melting point [of 12-hydroxy stearin acid]: — 80 degrees C and melting point: 160 degree C of a JIBEN zylidene sorbitol — as — the melting point was high generally, in solidifying short chain alcohols, it was unsuitable, for example, to organic solvents, such as general-purpose ethylene glycol, cellosolve, and ethanol, it dissolved industrially as a solvent of a low-boiling point, and it begins by adding very a lot of gelling agents thru/or solidification agents, can solidify, and was unsuitable to solidification of this organic solvent.

[0004] On the other hand, although there is "an AKUA rucksack CA" by Nippon Shokubai Kagaku Kogyo Co., Ltd., for example as an acrylic-acid system polymer as a gelling agent of the type of (2) and this solidifies almost all the hydrocarbons system compound, to an ester system compound or alcohols, there is no **** about the effectiveness of gel solidification. And this type of thing was difficult for obtaining a uniform gel object, in order to make the so-called gelled object absorb in a gelling agent and to solidify to the things of the aforementioned (1) type being melting and a thing to solidify about a gelling agent and a gelled object.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the gelation or the solidification agent which makes liquefied alcohol (however, with a carbon numbers of four or more monohydric alcohol is removed) with a gel uniform and smooth desirable solidification object in ordinary temperature.

[0006]

[Means for Solving the Problem] In order to attain said purpose, this invention persons came to complete a header and this invention for the gel object or solidification object of said alcohol being obtained by using a specific esterification product, as a result of repeating examination wholeheartedly. That is, this invention is the gelation or the solidification agent of liquefied alcohol (however, with a carbon numbers of four or more monohydric alcohol is removed) characterized by providing the following at ordinary temperature. A glycerol or its condensate (henceforth a glycerol etc.) Straight chain-like saturated fatty acid of carbon numbers 18-28 (only henceforth a fatty acid) The partial esterification product which is an esterification product with the aliphatic series saturation dibasic acid (only henceforth a dibasic acid) of carbon numbers 20-28, and was made to remain exceeding one half of hydroxyl groups, such as said glycerol

[0007] As an indispensable raw material component for manufacturing the esterification product of this invention, there is a glycerol etc. first. In this invention, average degree of polymerization says two or more things, five or more things are desirable still more desirable, and average degree of polymerization is about ten polyglycerin, and can specifically illustrate diglycerol, triglycerol, a PENTA glycerol, a hexa glycerol, a deca glycerol, etc., and the condensate of a glycerol can especially use these as independent or mixture.

[0008] Next, a fatty acid, i.e., a monobasic acid, makes it indispensable for a carbon number to be the straight chain-like saturated fatty acid of 18-28. Stearin acid, 10-hydroxy stearin acid, 10-keto stearin acid, 12-hydroxy stearin acid, arachin acid, a HEBEN acid, a montanoic acid, etc. can be raised as an example as concrete straight chain-like saturated fatty acid, and in this invention, even if it uses these with independent or mixture, it does not interfere. The esterification product stops easily being able to solidify target alcohol [be / the carbon number of this fatty acid / less than 18] due to this invention.

[0009] Moreover, as a dibasic acid, a carbon number needs that it is the thing of the letter of aliphatic series saturation of 20-28. The thing or carbon number of partial saturation cannot obtain easily the dibasic acid to which, as for the esterification product of less than 20 dibasic acid, a carbon number exceeds 28 by gelation ability falling as a industrial raw material. therefore, independent [in dibasic acids such as eicosa dicarboxylic acid, a docosa KOSAJI carboxylic acid, tetracos a dicarboxylic acid, hexacos a dicarboxylic acid, and OKUTAKOSA dicarboxylic acid] in this invention — or OKUTAKOSA dicarboxylic acid can be easily isolated from oil seeds including the Goma seed, and is [that what is necessary is just to use it, mixing] suitable.

[0010] What is necessary is just to adopt either of the approaches described below, in order to be able to combine said raw material suitably, to be able to use it and to obtain the esterification product of this invention. that is, a glycerol etc. carries out the oligo esterification reaction of a fatty acid and the dibasic acid to coincidence, or a glycerol etc. and a fatty acid are esterified first — making — this — further — a dibasic acid and an oligo esterification reaction — or an ester exchange reaction is carried out, or oligo esterification of a glycerol etc. and the dibasic acid is carried out first, and, subsequently the esterification reaction of this is carried out to a fatty acid.

[0011] Under existence of an acid, alkali, or a metal catalyst or nonexistence, in an organic solvent desirable and inactive for this reaction, or/and a gas, an esterification reaction removes the water which carries out a byproduction for several hours to 20 hours, and performs it at 100-240 degrees C. Moreover, an ester exchange reaction is performed at 20-140 degrees C for dozens of minutes to dozens hours using catalysts, such as a metal alcoholate or lipase. Said reactivity can be evaluated by measuring the presentation of the acid number in a system, or the acid component of a free state, and, thereby, should just determine the termination time of a reaction. Since a fatty acid and the fatty acids which may contain a dibasic acid, in addition carry out a byproduction, such as an unreacted glycerol, the glyceride of low molecular weight, etc. may be intermingled, esterification or an ester exchange reaction object will carry out separation removal of these by well-known approaches, such as rinsing and alkali deoxidation, if it requires, and if it requires further, decolorization and deodorization processing will be performed and it will refine them.

[0012] The esterification products of this invention obtained in this way are mixture with which oligo esterification of a fatty acid and the

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dibasic acid was carried out at the shape of the shape of a straight chain, and a mesh, such as a glycerol, and the melting point is about 50-80 degrees C. In addition, the residual hydroxyl group of an esterification product makes it indispensable to make it remain across the one half of hydroxyl groups, such as a glycerol which is a raw material. If a residual hydroxyl group becomes below one half, compatibility with target alcohol will be inferior by this invention, and a uniform and smooth gel solid will not become. From the reaction mol equivalent of the reaction mol equivalent and fatty acids, such as the blending ratio of coal of a raw material, i.e., a glycerol etc., and a dibasic acid, the hydroxyl value of the esterification product of this invention can be computed easily, and can be adjusted. Moreover, it can adjust also by the existence of purification of reaction temperature, reaction time, and a reactant.

[0013] the esterification product of this invention is independent in this — or it can mix and can make in ordinary temperature with the gelling agent of liquefied alcohol (however, with a carbon numbers of four or more monohydric alcohol is removed), or a solidification agent. As target alcohol, by this invention here A with a carbon number of three or less methanol, ethanol, 1-propanol, 2-propanol, Others [monohydric alcohol /, such as ethylene glycol monomethyl ether,], Ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, 1,3-butanediol, 1,4-butanediol, Glycerylmonoacetate, a glycerol, triglycerol, a hexa glycerol, Liquefied fluorination alcohol etc. can be illustrated in nitrogen-containing alcohol, such as polyhydric alcohol, such as a deca glycerol, monoethanolamine, dipropanolamine, and triethanolamine, and ordinary temperature. In addition, it is hard to solidify by gelation or the solidification agent of this invention, and with a carbon numbers of four or more monohydric alcohol is not suitable as an object.

[0014] if it adds five to 7% of the weight and the esterification product of this invention is preferably required three to 15% of the weight to said alcohol — about 80 degrees C — warming — after melting — light — stirring — ordinary temperature — **** — it is — if it cools and puts on about 5 degrees C gently, it will be uniform and a smooth gelation object or a smooth solidification object with viscosity nature thru/or a gel solidification object will be obtained. The whole system holds a homogeneity condition, without this thing generating a liquid part in ordinary temperature. In addition, gelation or the solidification agent of this invention may blend independent or the solid-state fat which becomes this from glycerides, such as a palmitic acid besides being waxes with conventionally still better known optimum dose, for example, carnauba wax, a candelilla wax, a montan wax, a micro crystallin wax, paraffin wax, etc., stearin acid, and behenic acid, unless it deviates from the purpose of this invention, although only mixture does not interfere of said esterification product. Moreover, you may use together with said well-known gelling agent.

[0015]

[Example] In the following synthetic examples and examples, % is weight criteria.

Deca glycerol 75g (0.1 mols), 85g (0.3 mols) of stearin acid, and 17g (0.05 mols) of eicosa dicarboxylic acid were taught to the 4 Thu openings flask furnished with synthetic example 1 agitator, a thermometer, gas blowing-in tubing, and a water separator, xylene 5% was added as 0.1% of p-toluenesulfonic acid, and a reflux solvent as a catalyst, and among the nitrogen gas air current, the esterification reaction was performed for 10 hours until the fall of the acid number was no longer accepted at 180-230 degrees C. Deodorization processing by decolorization and steam blowing in was performed by rinsing and activated carbon after reaction termination, and 138g (sample notation: referred to as A) of esterification products of this invention was obtained. this thing — acid-number: — they were 0.4, hydroxyl value:264, and melting point:62-67 degree C.

[0016] 17g (0.05 mols) of eicosa dicarboxylic acid was added to 2deca glycerol 75g (0.1 mols) of synthetic examples, and 37g (0.1 mols) of behenic acid, the esterification reaction was performed like the synthetic example 1, purification processing was carried out, and 101g (sample notation: referred to as B) of esterification products of this invention was obtained. this thing — acid-number: — they were 0.6, hydroxyl value:409, and melting point:66-69 degree C.

[0017] Synthetic example 3 PENTA glycerol 39g (0.1 mols) and 85g (0.2 mols) of montanoic acids were esterified with the conventional method, and the partial esterification object was obtained. The insoluble matter which is made to distribute and dissolve the approach of a Japanese Patent Application No. [for which these people applied previously / No. 230734 / five to] publication, i.e., the settlings of the Goma crude oil, (cage) in ethanol on the other hand, and cools and deposits is separated. Having added 28g (0.06 mols) of obtained OKUTAKOSA dicarboxylic acid to said partial esterification object, having added lipase (the Meito Sangyo Co., Ltd. make, lipase QL) 1% of opposite raw materials, and stirring at 120 degrees C, the gas chromatography analyzed the content of the montanoic acid which carries out a byproduction, and the ester exchange reaction was performed for 50 hours until the increment was no longer accepted. After reaction termination, purification processing was carried out like the synthetic example 1, and 116g (sample notation: referred to as C) of esterification products of this invention was obtained. this thing — acid-number: — they were 0.8, hydroxyl value:145, and melting point:67-73 degree C.

[0018] The esterification product (sample notation: A-C) obtained in the examples 1-3 of example 1 composition, 12-hydroxy stearin acid, and the solidification ability to the ethanol of carnauba wax were examined. The result is shown in Table 1. In addition, after heating and fusing the examining method at 70 degrees C, taking and stirring ethanol and 7% of each of its sample to a beaker and cooling radiationally in ordinary temperature as it is for 3 hours, the condition of the obtained solid was observed. evaluation — O: — hard, uniform, and smooth gelation or a solidification object, and O: — uniform and smooth gelation or a solidification object, and **: — the part considered as what carries out solid liquid separation, and the thing of which x:solidification is not done.

[0019]

[Table 1]

表1 エタノールの固形化物

| | 本発明例 | | | 比較例 | |
|------------|------|-----|-----|--------------------|---------------|
| 添加物 | 試料A | 試料B | 試料C | 12-ヒドロキシ ステアリン酸 | カルバウバ ワックス |
| 固形物の 状態 | ◎ | ◎ | ◎ | × | × |

[0020] It became clear that the esterification product (sample notation: A-C) of Table 1 to this invention forms the gel object or solidification object which has uniform and smooth viscosity nature to ethanol in spite of being little addition compared with a conventional gelling agent and a conventional wax. Moreover, when these were saved for one month in ordinary temperature, what added the esterification product of this invention was maintaining the homogeneity condition, and the stable thing was accepted. In addition, 12-hydroxy stearin acid and carnauba wax were not able to solidify ethanol with this addition.

[0021] The solidification ability to the various alcohol of the esterification product (sample notation: B) obtained in the example 1 of example 2 composition was investigated by the same approach as an example 1. The result is shown in Table 2. In addition, the sign of evaluation is the

same criteria as an example 1. From Table 2, esterification product of this invention was little, and had gelation or solidification ability to various alcohol, and, moreover, each solid was presenting description with uniform and smooth viscosity nature.

[0022]

[Table 2]

表2 各種アルコールの固化物

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| アルコールの種類 | 試料Bの添加率と固形物の状態 | | |
|-------------|----------------|-----|-----|
| | 3 % | 5 % | 7 % |
| メタノール | △ | ○ | ◎ |
| エタノール | △ | ○ | ◎ |
| 1-プロパノール | △ | ○ | ◎ |
| 2-プロパノール | △ | ○ | ◎ |
| エチレングリコール | △ | ○ | ◎ |
| プロピレングリコール | △ | ○ | ◎ |
| 1,4-ブタンジオール | △ | ○ | ◎ |
| グリセリン | △ | △ | ○ |
| n-ブタノール | × | × | × |

[0023]

[Effect of the Invention] According to this invention, they are a glycerol or its condensate, and the straight chain-like saturated fatty acid of carbon numbers 18-28, The partial esterification product which is an esterification product with the aliphatic series saturation dibasic acid of carbon numbers 20-28, and was made to remain exceeding one half of the hydroxyl groups of said glycerol or its condensate is obtained, and the stable gelation or the solidification object which has homogeneity and smooth viscosity nature only by carrying out little addition of this in ordinary temperature at liquefied alcohol (however, with a carbon numbers of four or more monohydric alcohol being removed) can be formed. Therefore, the esterification product of this invention can be made with the gelling agent of said impossible alcohol, or a solidification agent with a conventional gelling agent and a conventional wax, and this gelation or a solidification agent can be effectively utilized in a solvent processing agent, a release agent, adhesives, a binder, a sealing agent, the coating, a paint film agent, a volatile-component modifier, etc.

[Translation done.]